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BASIC TECHNOLOGICAL PRINCIPLES AND GLASSMAKING

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The basic principles of technology as applied to glassmaking are examined. It is shown that viscosity plays the determining role. The principles of best use of raw and other materials, the driving force of processes, energy resources, assemblies and equipment while adhering to technological commensurability are discussed from physical-chemical and technological standpoints. Promising directions of development of glass furnace design are briefly examined from the standpoint of chemical technology and basic technological principles.

Key words: glassmaking, viscosity, technological principles, process rate, glassmaking efficiency.

The problem of technology as a science is to find the physical-chemical, mechanical and other regularities in order to determine and use in practice the most efficient and cost-effective production processes, requiring the least amount of time, material and energy resources and securing worker safety and economic and ecological efficiency [1 – 3].

As a rule, real technological processes in glass production are complex and consist of a collection individual, narrower processes and phenomena: physical-chemical, thermal, mass-transfer and others.

General Technological Principles. For a process to be as cost-effective as possible it must pass through all stages as quickly as possible and make full use of the raw materials or other initial products with minimal energy consumption and maximum production per unit of equipment. These problems lead to the following general technological principles which are based on best usage:

– driving force of the process;
– raw and other materials;
– energy resources;
– assemblies and equipment;
– technological commensurability (elimination of contradictions arising with the application of the first four principles; optimization of the technological parameters that secure worker safety and economic and ecological efficiency of the process).

These general technological principles are examined in application to glassmaking.

Process Rates. The technological processes involved in glassmaking are usually very complex, and often their rates are determined by an entire collection of conditions for the flow of not only chemical reactions but also a number of physical processes which are also associated with hydrodynamics, heat and mass transfer and others.

The characteristics of the process rates must without fail be taken into account at the time the technological assemblies are being designed. The regularities of rate variations for the main process groups can be formulated in the form of a general law: the rate of a process is directly proportional to the driving force of the process:

for chemical processes:

$$\mathrm{d}M/V\,\mathrm{d}\tau = k_1 f(a, C, t), \tag{1}$$

where M is the amount of matter which has undergone a reaction in the chemical process (or the degree of transformation of matter); V is the volume of the reaction zone or assembly; $f(a, C, t)$ is the average driving force of the process, which is a function of the chemical affinity a of the components, the concentrations C of the reactants (or the content of the components in a complex mixture of raw materials — the batch) and temperature t;

for heat transfer:

$$\mathrm{d}Q/F\,\mathrm{d}\tau = k_2\,\Delta t,$$

where Q is the amount of heat which has been transferred; F is the surface area of heat transfer; and Δt is the average temperature difference;

for transfer of matter from one phase into another:

$$\mathrm{d}M/F\,\mathrm{d}\tau = k_3\,\Delta C,$$

where M is the amount of matter transferred from one phase into another; F is the interphase contact surface area; and, ΔC is the concentration difference between the phases;

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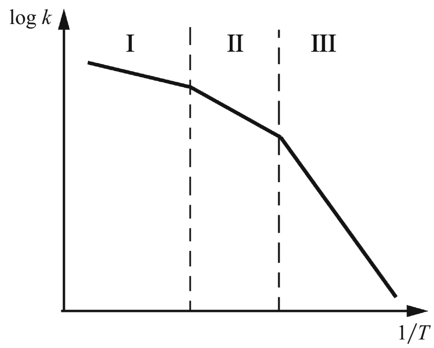

Fig. 1. Rate constant of a chemical reaction versus the temperature: I) diffusion region; II) transient region; III) kinetic region.

for the materials (liquid or gas) flow:

$$dV/F\,d\tau = k_4 \Delta p,$$

where V is the volume of the flowing liquid (melt) or gas; F is the transverse area of an assembly or the corresponding zone; Δp is the pressure drop in the assembly or corresponding zones.

In the relations presented $k_1 - k_4$ are process rates (constants) and τ is the time.

Physical-Chemical Interaction Conditions. A technological process with chemical interaction can be divided into a series of elementary interaction processes:

– delivery of the reactants into the chemical reaction zone;

– chemical interaction of the components;

– removal of the products formed in interactions out of the chemical reaction zone.

The total rate of a process is determined by the rate of the elementary stages enumerated above, which can differ considerably. For this reason, the total rate of a process is limited by the rate of the slowest stage [4].

If the slowest reaction is a chemical reaction and it limits the total rate, then the process proceeds in the *kinetic* region. To accelerate such processes the technological factors having the strongest effect on the rate of the chemical reaction, taking account of, for example, the temperature and concentration, using catalysts.

If the delivery of reactants or removal of the reaction products limits the total rate of a process, then the process proceeds in the *diffusion* region. To accelerate such processes efforts are made to increase diffusion by intensifying mixing and increasing temperature.

If the rates of the stages of a technological process are comparable, then the process proceeds in the *diffusion-kinetic* (transitional) region. To increase the rate of such a process it is necessary to act on the system via factors which increase the rate of diffusion as was as the rate of the chemical reaction, for example, by increasing the temperature.

Figure 1 shows the dependence of the rate constant of the transformation occurring first on the temperature for the diffusion, kinetic and diffusion-kinetic regions of the process flow. Then the transformation rate constant is determined by the tangent of the slope angle of a straight line relative to the abscissa. The character of the dependence indicates that as the temperature in the system increases a transition is observed from the kinetic into the diffusion region; the effect of the temperature on the rate of the transformation into the kinetic region is much stronger than in the diffusion region. At high temperatures the chemical interaction occurs very rapidly and the limiting stage becomes the diffusion process, which can be activated by creating convective flows during mixing.

According to [4], the overall process rate constant for the diffusion-kinetic regime is given by the relation

$$K = \frac{k_1 k_2}{k_1 + k_2}, \tag{5}$$

where k_1 and k_2 are the rate constants of the chemical reaction and diffusion process, respectively.

The relation (5) makes it possible to determine the limiting regions of the diffusion-kinetic process. For $k_1 \ll k_2$, $K \approx k_1$ the process proceeds in the kinetic region and for $k_1 \gg k_2$, $K \approx k_2$ in the diffusion region.

Glassmaking. For the most massive articles the glassmaking process proceeds at temperature 1480 – 1550°C. The batch is loaded into the zone of maximum temperature and the initial stages of the chemical reactions of the Na_2CO_3 melt with SiO_2 and other components of the batch proceed very rapidly. The viscosity of the melt increases significantly at the same time. In accordance with Fig. 1 the chemical interaction transitions from the kinetic into the diffusion region and subsequently the viscosity of the melt determines the interaction rate. The results obtained by E. Preston, which are displayed in Fig. 2, with Na_2O–CaO–SiO_2 glasses attest to this [5]. Here the rate of glass formation is denoted as the time when melt with no batch residues is obtained. As is evident from the figure, the courses of the curves are very similar and the correspondence between the glass-formation rate (time) is completely obvious.

Thus, the high viscosity of the glass-forming melts decreases the driving force for the glass-making process, which results in high energy consumption. A number of questions concerning commercial glassmaking are examined in [6].

Raw materials usage. The cost of raw and other materials in the manufacture of glass articles is a large part of the production costs. Thus, in the manufacture of sheet glass, glass containers and housewares the raw-material and materials fraction in the production costs is 16 – 40%; in addition, ordinarily, for sheet-glass and containers this fraction is even higher for the manufacture of housewares. In planning and organizing production raw and other materials must be used fully and effectively. The ways for using materials in the glass industry effectively are diverse. Since glass works now obtain completely ready raw materials, the principal utilization paths are as follows:

– proper organization of transport and storage of raw and other materials at the enterprise in order to preserve the quality and prevent loss of materials;

– comprehensive use of raw materials, production wastes and secondary resources;

– reduction of the materials content of the manufactured product while maintaining operational reliability (glass containers).

A significant factor in raw-materials conservation in the glass industry, especially in the production of glass containers, is the use of cullet. Centralized collection and preparation of cullet make it possible in individual cases to use to 50 – 70% and event 100% cullet in the production of colored container glass, which substantially reduces raw materials costs.

A very important problem in the glass industry is to make full use of the raw materials and production wastes. The value of readily available raw materials is increasing while together with accessibility and low cost such materials have technological advantages. The use of different rocks is characteristic for the manufacture of sheet glass and glass containers. Specifically, nepheline, feldspar and pegmatite concentrates with a constant composition, which are products of ore enrichment, are used to introduce Al_2O_3 into glass. Together with Al_2O_3 other glass forming oxides (SiO_2, CaO, MgO, K_2O, Na_2O) are also introduced with them; this conserves the corresponding raw materials (sand, dolomite, soda).

Homogenized and purified metallurgical slags (calumite) are used effectively in the manufacture of different types of glass and glass articles. This makes it possible not only to conserve raw materials but also to intensify the glassmaking process [7, 8]. Calumite can be used in amounts to 8% in the production of sheet glass and to 20% in the production of glass fiber and colored glass containers. In Russia there is also experience in using metallurgical slags — at the Chagodoshchenskii and Lipetsk glass container works, where metallurgical slags from the nearby Cherepovets and Lipetsk metallurgical works are used. The Borskii Glass Works uses calumite from Czechoslovakia in the production of float-glass.

Unfortunately, centralized processing and production of valuable raw materials based on metallurgical slags has still not been organized in Russia.

Energy usage. The production of glass and glass articles is energy-intensive. The fraction of different forms of energy in the cost of production is quite large, glass furnaces consuming the most energy (60 – 75%).

The theoretical heat consumption per 1 kg Na–Ca–Si glass made from batch is 2660 kJ. For cullet this figure decreases to 1900 kJ. The heat used for glassmaking in practice is considerably higher than the theoretical amount, especially for flame furnaces; this is due to the relatively low efficiency of these furnaces. The main directions for increasing the energy use efficiency of flame furnaces involve efficient organization of fuel burning, air-tightness and heat-insulation of furnace enclosures and increasing the operating efficiency of re-generators and recuperators. The efficiency of glass furnaces can be increased by addition electric heating in flame glass furnaces. The most efficient furnaces are purely electric glass furnaces, because in them energy is released inside the melt and is used for glassmaking to the fullest possible extent.

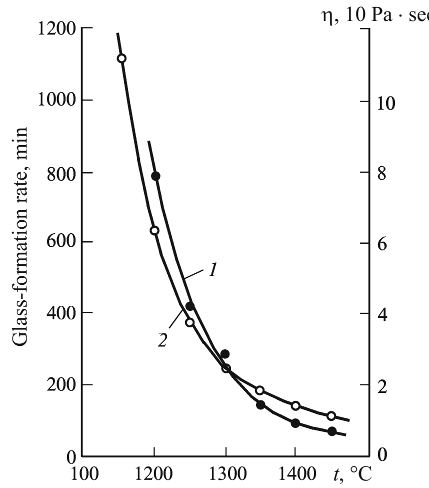

Fig. 2. Relation between the glass-formation rate (time) (*1*) and glass viscosity (*2*).

A great deal of experience in increasing the efficiency of glassmaking has been accumulated in foreign and domestic glass industries. As a result, fuel consumption in flame furnaces has decreased considerably and the useful heat consumption fraction has increased. The overall efficiency of such furnaces can reach 50 – 60% and that of electric furnaces 80%.

The basis for determining the consumption of energy and fuel and to determine the directions for increasing the operating efficiency of furnaces are the energy (heat) balances which are constructed in heat-engineering calculations of furnaces [9, 10].

The utilization of the heat in the exhaust gases of glass furnaces after regenerators and recuperators (with the appropriate heat-exchange apparatus) for heating batch and cullet, drying materials, space heating, hot water for industrial and administrative buildings increases the heat-use efficiency.

There is also room for electricity conservation. This requires efficient operation of the process equipment and optimization of the power levels of electric motors and other electric equipment.

Assembly and equipment usage. The main assembly in glass manufacture is the glassmaking furnace, in which high-temperature physical-chemical processes where mixtures of crystalline raw materials (batch) are converted into a glass-forming melt that is suitable for the production of the corresponding articles.

In chemical technology relatively low-temperature processes are classified according to the predominant indicators of the chemical-technological process: chemical, mass-trans-

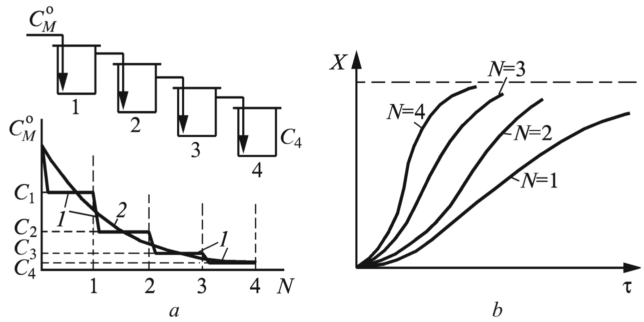

Fig. 3. Step (*1*) and average (*2*) change of the concentration C of the initial material (*a*) and its degree of transformation (*b*) in a cascade of reactors ($N = 1 ... 4$): X) degree of transformation; τ) time.

fer, thermal and hydromechanical. Equipment permitting full use of the main technological principle — the driving force of the process — is designed accordingly.

A glass furnace does not meet these conditions, because such a furnace is a unified assembly with a common tank and a flame space where the processes occur (silicate formation, glass formation, fining, and homogenization), requiring different, most efficient technological regimes. In glass furnaces, especially those used for massive articles, these stages are not clearly separated and the corresponding regimes are not sharply established. As a result the furnaces are disproportionately large and they operate inefficiently from the standpoint of modern technologies and environmental protection.

In low-temperature chemical technology the technique of sectioning is used to increase the driving force of the process, i.e., the working volume of the mixing apparatus is divided into sections. In so doing a cascade of reactors with comparatively low degree of transformation at each step is formed.

Figure 3 shows the variation of the concentration of the initial substances and the degree of transformation versus the number of reactors in a cascade. Different operating regimes, specifically, temperature and hydrodynamic, must be established in each reactor. As a result of an increase of the driving force of the process the time to the prescribed degree of transformation is reduced. These dependences can also be applied to the vitrification process, if the content of the solid phase (batch) is used instead of the concentration and the amount of the glass-forming melt obtained is used as the degree of transformation.

Glass furnace designs and methods for intensifying glassmaking were improved over a long period of time. Glass furnaces now incorporate means of intensification such as high-temperature regimes, electric heating, oxygen for gas combustion, and hydrodynamic conversion systems (mixers, swirling). To conserve energy efficient fuel burning regimes have been adopted and high-quality refractories and thermal insulation are used. Facilities for utilizing the heat contained in the exhaust gases are effective. As a rule, the glassmaking process has been automated, and computer control has been introduced. The service life of furnaces now reaches 10 or more years because highly stable refractories and knowledgeable operation are used [6].

However, these methods of intensifying glassmaking do not completely solve the problems of combining the overall production efficiency, energy conservation, and environmental protection. In this connection, the scientific-technical solutions for the problems of glassmaking must be of an all-encompassing nature and simultaneously remove the indicated problems. One solution is to use free burners and contact ignition of the gas in the molten glass. Commercial tests performed in the USA have made it possible to attain specific production equal to approximately 5.5 tons/day, specific energy consumption 3376 kJ/kg molten glass and substantial reduction of gas dust emissions as well as sharp reduction of glass-furnace dimensions. Apparently, in the future the melting tanks in furnaces will consist of separate standard sections or modules where the processes will reflect the staged character of the glass-making process. Thus, the development of glassmaking will proceed in the direction of applying the experience gained in low-temperature chemical technology.

Process efficiency and technological commensurability. When new technological processes are adopted in production or changes are made in an existing technological process the comparative economic efficiency, which characterizes the economic advantages of one variant over others, is usually determined. Before the economic efficiency of technological processes is determined questions concerning the technological commensurability or optimization of technological solutions must be resolved. The problem is that the application of the technological principles examined often leads to contradictory results.

We shall now examine some examples from the field of commercial glassmaking.

The use of rocks or industrial wastes in the manufacture of sheet glass and glass containers leads to efficient use of raw materials. However, to obtain high-quality glass and articles questions concerning the chemical composition of the raw materials and its constancy, the amount introduced into the batch, cost and so forth must be examined.

Raising the glassmaking temperature in gas-flame furnaces intensifies the glassmaking processes substantially. However, above 600°C considerable wear of the refractory masonry of a furnace is observed, problems of effective cooling of the molten glass to extraction temperatures arise, and the products of combustion become enriched with toxic nitrogen oxides which contaminate the environment. The use of electricity for melting greatly intensifies the glassmaking process but electricity is substantially more expensive than natural gas. However, in each individual case the economic indicators must be scaled to the social and ecological indicators. For example, the use of purely electric melting in the manufacture of lead crystal and borosilicate glass is completely justified because the losses of volatile components, first and foremost lead oxides, which contaminate the envi-

ronment, are reduced, the glass furnace is smaller, and the production culture improves. However, in sheet-glass and container glass manufacture purely electric glassmaking is still not only technically difficult to accomplish but it is economically unprofitable because of the high cost of electricity. Good results in the manufacture of such products can be attained with partial use (5 – 15%) of electricity.

The complexity and diversity of technological processes involved in glass production as well as a definite imperfection of the technology and equipment call for a deeper study of the physical-chemical and technological particularities of the production processes. The general principles indicate the direction of analysis of the technological process as a whole as well as its individual stages for increasing production efficiency.

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